5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

The most important natural starting material for the production of fluorine chemicals, including fluorine, hydrogen fluoride, and sodium fluoride, is the mineral fluorite (calcium fluoride [CaF_2]), commonly called fluorspar. Other important fluorine minerals are fluorapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6). There has been no fluorspar mine production in the United States since 1996; supplies were imported or purchased from the National Defense Stockpile. In addition, some byproduct calcium fluoride was recovered from industrial waste streams. An estimated 8,000–10,000 metric tons of fluorspar are recovered each year from uranium enrichment, stainless steel pickling, and petroleum alkylation. To supplement fluorspar supplies, fluorosilicic acid is recovered from phosphoric acid plants processing phosphate rock. In 1999, 69,100 tons of byproduct fluorosilicic acid (equivalent to 122,000 tons of fluorspar) was produced by 10 plants owned by 5 companies. In 1999, the main fluorspar-producing countries, in order of importance, were China, Mexico, Russia, Spain, and France. The apparent consumption of fluorspar (excluding fluorspar equivalents of fluorosilicic acid, hydrofluoric acid, and cryolite) in the United States was 615,000 metric tons in 1999 and was estimated to be 612,000 metric tons in 2000 (USGS 2001). Approximately 60–65% of the fluorspar consumed goes into the production of hydrogen fluoride. Large amounts are also used as a flux in steel production.

Fluorine is produced commercially by electrolyzing anhydrous hydrogen fluoride containing dissolved potassium fluoride to achieve adequate conductivity (Jaccaud and Faron 1988; Shia 1994). Potassium fluoride and hydrogen fluoride form potassium bifluoride (KHF_2 or $KF \cdot HF$). Fluoride is oxidized at the anode, producing fluorine, and the hydrogen ion is reduced at the cathode, producing hydrogen gas. Information concerning the amount of fluorine produced is not available. The commercial fluorine production capacity of the United States and Canada is over 5,000 tons/year (Shia 1994).

Anhydrous hydrogen fluoride is manufactured by the action of sulfuric on calcium fluoride. Powdered acid-grade fluorspar ($97% CaF_2) is distilled with concentrated sulfuric acid; the gaseous hydrogen fluoride that leaves the reactor is condensed and purified by distillation (Smith 1994). The U.S. capacity for hydrogen fluoride production was 198,000 metric tons in 2000 (SRI 2000). The demand for hydrogen fluoride, which was 340,000 metric tons in 1998, is expected to increase to 390,000 metric tons in 2002 (CMR 1999).

Sodium fluoride is manufactured by the reaction of hydrofluoric acid with sodium carbonate or sodium hydroxide. The salt is centrifuged and dried (Mueller 1994). Information concerning the amount of sodium fluoride produced is not available.

Current U.S. manufacturers of fluorine, hydrogen fluoride, and sodium fluoride are given in Table 5-1. Tables 5-2 and 5-3 list the number of facilities in each state that manufacture, process, or use hydrogen fluoride and fluorine, respectively, their intended uses, and the range of maximum amounts of these substances that are stored on-site. In 1999, there were, respectively, 1,022 and 14 reporting facilities that produced, processed, or used hydrogen fluoride or fluorine in the United States. The data listed in Tables 5-2 and 5-3 are derived from the Toxics Release Inventory (TRI99 2001). Only certain types of facilities were required to report. Therefore, this is not an exhaustive list. Sodium fluoride or other fluoride salts are not listed on TRI.

5.2 IMPORT/EXPORT

In 1999, the United States imported 419,000 metric tons of acid grade (>97%) fluorspar and 59,000 metric tons of metallurgical-grade (<97%) fluorspar (USGS 2001). This importation was supplemented by the fluorspar equivalent of 192,000 metric tons from hydrofluoric acid plus cryolite. The estimated imports of fluorspar for 2000 were 510,000 metric tons of acid-grade, 41,000 of metallurgical-grade, and 215,000 tons from hydrofluoric acid plus cryolite. Between 1996 and 1999, 67% of fluorspar imports came from China, 22% from South Africa, and 11% from Mexico. Exports of fluorspar for 1999 were 55,000 metric tons (USGS 2001) and are estimated to fall to 48,000 in 2000. Exports consist of imported material that was reexported or material obtained from the National Defense Stockpile. In 2000, 43,000 metric tons of metallurgical-grade fluorspar from the stockpile were disposed of. In 1999, most of the exports were to Italy and Canada (USGS 1999).

U.S. imports for consumption are available for three other fluorides: hydrofluoric acid, cryolite, and aluminum fluoride. For 1999, these were 120,000, 9,560, and 19,300 metric tons, respectively. For hydrofluoric acid, 76% of imports came from Mexico and 22% from Canada.

5.3 USE

Fluorine gas is used captively for the production of various inorganic fluorides. The preparation of fluorides of an element in its highest oxidation state makes use of fluorine's oxidizing and fluorinating ability. The most important product is uranium hexafluoride (UF_6), which is used in the gaseous diffusion process for producing enriched uranium-235 for the nuclear industry. This use consumes 70–80% of fluorine production. The second most important product is sulfur hexafluoride (SF_6), which is used as a gaseous dielectric for electrical and electronic equipment and a tracer gas for determining ventilation rates and air movements in buildings. Other uses of fluorine include: the treatment of polyolefin containers to reduce their permeability to organic liquids; the treatment of a polymer surface for the application of an

Table 5-1. U.S. Manufacturers of Hydrogen Fluoride, Fluorine and Sodium Fluoride[a]

Company	Location	Annual capacity[b] (10^3 metric tons)
Hydrogen Fluoride[c]		
Dupont	La Porte, Texas	80
General Electric[d]	Geismar, Louisiana	118
Fluorine		
General Electric[d]	Metropolis, Illinois	
Sodium fluoride		
Chemtech Products Inc.	Alorton, Illinois	
Elf Atochem North America, Inc.	Tulsa, Oklahoma	
Mallinckrodt Baker Inc.	Phillipsburg, New Jersey	

[a]Derived from SRI 2000
[b]Plant capacity available only for hydrogen fluoride
[c]Merchant producers. Alcoa produces hydrogen fluoride as a nonisolatable product.
[d]Formerly Honeywell, and before that, Allied Signal.

Table 5-2. Facilities that Produce, Process, or Use Hydrogen Fluoride

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AK	1	100	999	1, 5
AL	8	0	9,999,999	1, 5, 7, 12, 13
AR	5	0	999,999	1, 5, 6, 7, 8, 12
AZ	13	0	999,999	1, 5, 6, 7, 8, 10, 11, 12, 13
CA	21	0	49,999,999	1, 2, 3, 4, 7, 8, 10, 11, 12, 13
CO	5	0	999,999	1, 5, 8, 10, 12, 13
CT	3	1,000	99,999	1, 5, 11, 12, 13
DE	2	0	999,999	1, 5, 7
FL	15	0	999,999	1, 3, 5, 6, 7, 8, 10, 11, 12, 13
GA	10	0	999,999	1, 5, 6, 8, 12, 13
HI	1	1,000	9,999	12
IA	6	0	999,999	1, 5, 6, 13
ID	5	100	999,999	1, 5, 6, 11, 12, 13
IL	20	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13
IN	11	0	99,999	1, 3, 5, 8, 11, 12, 13
KS	5	0	9,999,999	1, 5, 6, 7, 8, 11
KY	12	0	9,999,999	1, 2, 3, 5, 7, 10, 11, 12, 13
LA	13	0	9,999,999	1, 2, 3, 4, 5, 7, 11, 12, 13
MA	7	0	99,999	1, 5, 11, 12, 13
MD	2	0	999	1, 5
ME	2	1,000	9,999	11, 12
MI	14	0	999,999	1, 2, 5, 7, 8, 11, 12, 13
MN	4	0	99,999	1, 5, 7, 11, 12, 13
MO	7	0	99,999	1, 5, 6, 12, 13
MS	6	0	9,999,999	1, 5, 6, 8, 12
MT	5	0	999,999	1, 5, 11
NC	11	0	999,999	1, 5, 6, 7, 12, 13
ND	4	0	999,999	1, 5, 6, 11
NE	3	0	99,999	1, 5, 6
NH	3	0	99,999	1, 5, 12, 13
NJ	10	0	9,999,999	1, 2, 3, 5, 7, 8, 11, 12, 13
NM	6	0	999,999	1, 5, 6, 11, 12

Table 5-2. Facilities that Produce, Process, or Use Hydrogen Fluoride *(continued)*

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
NV	3	0	999,999	1, 2, 3, 5, 9
NY	14	0	9,999,999	1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13
OH	19	0	999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13
OK	10	0	99,999,999	1, 2, 3, 5, 6, 7, 8, 10, 11, 13
OR	14	0	999,999	1, 2, 3, 4, 5, 10, 11, 12, 13
PA	23	0	49,999,999	1, 2, 3, 5, 6, 7, 8, 10, 11, 12, 13
PR	3	100	999,999	7, 12
RI	3	100	99,999	7, 12, 13
SC	11	0	999,999	1, 3, 5, 7, 11, 12, 13
SD	2	0	9,999	1, 5, 12
TN	7	0	999,999	1, 2, 5, 6, 11, 12, 13
TX	30	0	49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13
UT	9	0	999,999	1, 5, 6, 7, 11, 12, 13
VA	6	0	999,999	1, 5, 11, 12, 13
VT	2	1,000	99,999	12
WA	8	0	999,999	1, 3, 5, 11, 12, 13
WI	11	0	999,999	1, 5, 6, 8, 11, 12, 13
WV	5	0	999,999	1, 2, 3, 5, 11, 12
WY	5	0	999,999	1, 2, 3, 5, 11, 12

Source: TRI99 2001

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses

Table 5-3. Facilities that Produce, Process, or Use Fluorine

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	1	0	99	1, 6
GA	1	0	99	1, 5
IL	1	10,000	99,999	1, 3, 7
KS	1	0	99	1, 5, 13
LA	1	1,000	9,999	1, 3, 7, 13
MD	1	10,000	99,999	9
NC	3	10,000	999,999	9
NJ	1	100	999	2, 3, 7
OK	1	100,000	999,999	9
PA	1	1,000	9,999	1, 3, 4, 7, 10
PR	1	1,000	9,999	12
TX	1	1,000	9,999	13

Source: TRI99 2001

[a]Post office state abbreviations used
[b]Amounts on site reported by facilities in each state
[c]Activities/Uses:

1. Produce
2. Import
3. Onsite use/processing
4. Sale/Distribution
5. Byproduct
6. Impurity
7. Reactant
8. Formulation Component
9. Article Component
10. Repackaging
11. Chemical Processing Aid
12. Manufacturing Aid
13. Ancillary/Other Uses

adhesive or coating; and the production of some fluorinated organic compounds (Guo et al. 2001; Shia 1994).

Hydrogen fluoride is the most important compound of fluorine. Anhydrous hydrogen fluoride is used in the production of most fluorine-containing chemicals. It is used in the production of refrigerants, herbicides, pharmaceuticals, high-octane gasoline, aluminum, plastics, electrical components, and fluorescent light bulbs. Aqueous hydrofluoric acid is used in stainless steel pickling, glass etching, metal coatings, exotic metal extraction, and quartz purification (Hance et al. 1997). The most important use of hydrogen fluoride is in the production of fluorocarbon chemicals, including hydrofluorocarbons, hydrofluorochlorocarbons, and fluoropolymers; 60% of production is used for this purpose. Demand for hydrogen fluoride for fluorocarbons, broadly used as refrigerants, is increasing as a nonchlorinated alternative to ozone-depleting chlorofluorocarbons. (Production of fluorocarbons uses more hydrogen fluoride than production of chlorofluorocarbons.) The next most important uses of hydrogen fluoride are: chemical derivatives, 18%; aluminum manufacturing, 6%; stainless steel pickling, 5%; petroleum alkylation catalysts, 4%; and uranium chemicals production, 3%. Miscellaneous other uses include glass etching, herbicides, and rare metals (CMR 1999). Generally, the aluminum industry consumes 10–40 kg of fluoride per metric ton of aluminum produced. The AlF_3 used in aluminum reduction cells may be produced directly from acid-grade fluorspar or byproduct fluorosilicic acid, rather than from hydrogen fluoride. Anhydrous hydrogen fluoride is used as a catalyst in the petroleum alkylation, a process that increases the octane rating of petroleum. In uranium chemicals production, hydrogen fluoride is used to convert uranium oxide (yellow cake, U_3O_8) to UF_4 before further fluorination to UF_6.

One of the principal uses of sodium fluoride is the fluoridation of public water supplies for the prevention of dental caries. Generally, 1.5–2.2 mg of sodium fluoride is added per liter of water (0.7–1.0 mg/L as fluoride). Sodium fluoride may also be applied topically to teeth as a 2% solution to prevent tooth decay. It is also used as a flux for deoxidizing rimmed steel, as a component of laundry sours (removal of iron stains), and in the re-smelting of aluminum, manufacture of vitreous enamels, pickling of stainless steel, wood preservative compounds, casein glues, manufacture of coated papers, and heat-treating salts (Mueller 1994).

5.4 DISPOSAL

Fluorine gas can be disposed of by conversion to perfluorocarbons or fluoride salts. Because of the long atmospheric lifetimes of perfluorocarbons, conversion to fluoride salts is preferable. Industrially, the waste stream is scrubbed with a caustic solution, KOH or NaOH, and for dilute streams, allowed to react with limestone (Shia 1994). Adequate contact and residence time is essential in the scrubber to ensure complete neutralization of the intermediate oxygen difluoride to prevent it from leaving the scrub tower.

According to the TRI, in 1999, 58,400 pounds of fluorine were treated on-site and 20,400 pounds were treated off-site (TRI99 2001).

According to the TRI, in 1999, an estimated 582,000 pounds of hydrogen fluoride were transferred off-site, including to publicly owned-treatment works (POTWs), by 1,022 reporting facilities presumably for disposal (TRI99 2001). No fluorine was transferred off-site in 1999 by 14 reporting facilities. According to the TRI, in 1999, 99.3% of hydrogen fluoride that was recycled or treated was performed on-site (TRI99 2001). Of the hydrogen fluoride recycled, 142 million was performed on-site and 146,000 pounds was performed off-site. Of the hydrogen fluoride that was treated, 130 million pounds were treated on-site and 2.4 million pounds were treated off-site. No information was found concerning how hydrogen fluoride is generally treated for disposal.

No information was found regarding the disposal of sodium fluoride. It would appear from its use that most of it is disposed of in municipal landfills or POTWs.